# A Density Estimation Model for Molten Silicate Slags

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## ABSTRACT:

A density estimation model for molten silicate slags has been proposed. The molar volume of molten silicate slags was calculated from molar volume of pure component and mixing molar volume, whereas the mixing molar volume was estimated from Gibbs free energy of mixing, which can be calculated by Toop-Samis model. Optical basicity was also used to calculate the equilibrium constant for three types of oxygen. The present model enables us to reproduce the experimental values for silicate slags with a deviation within 3%. The optical basicity was found to work well for estimating the density of molten silicate slags.

**Keywords:** molten silicate slags; density; estimation model, optical basicity

## 1. INTRODUCTION:

Density is one of the important properties of metallurgical molten slags. Density values of molten slag are needed in momentum, heat and mass transfer simulations for metallurgical processes. However, accurate experimental data for all systems required are not available, mainly arising from difficulties at high temperature measurements. It is therefore worthwhile to develop a model for density estimation of molten slags.

Various models to estimate the density of molten slags have been proposed in literature. Most of these models are based on estimation of partial molar volume. A commonly used additive method /1/ calculates density according to the following equation:

$$\rho = \frac{\sum_i M_i X_i}{\sum_i \bar{V}_i},$$

where $M_i$ is the molar weight of slag component I, $X_i$ is the molar fraction of I, $\bar{V}_i$ is the partial molar volume of I; Bottinga and Weil proposed a model using constant partial molar volume of component. Bottinga *et al.* /2/ also presented a model in which the partial molar volumes of alumina-silica liquids were considered to be composition dependent. Mills and Keen /3/ developed a model where partial molar volumes of $Al_2O_3$, $SiO_2$ and are described by polynomial functions of composition. Recently, Persson *et al.* /4/ developed a model to calculated density from relative integral molar enthalpy of mixing. The comparison between calculated and measured values showed agreements.

The concept of optical basicity was firstly proposed by Duffy *et al.* /5/ and had wide applications in metallurgical industry. The most famous application of optical basicity is in the estimation of sulphide capacity /6/. Mills /7,8/ presented an optical basicity model for viscosity estimation, Ray and Pal /9/ further modified the Mills model to achieve a simpler calculation procedure. Ottonello *et al.* /10/ established the relationship between polymerization constant K in Toop-Samis model /11/ and optical basicity. They have used the relationship to describe thermodynamic properties of silicate melts well.

The present work will present an estimation method for density of molten silicate slags. The molar volume of silicate slags was calculated from molar volume of pure component and mixing molar volume. The mixing molar volume was estimated from Gibbs free energy of mixing. Toop-Samis structural model was employed to calculate Gibbs free energy of mixing. Optical basicity was used to estimate the equilibrium constant. The estimated values for several binary, ternary systems were compared with experimental values to verify the model.

## 2. THEORETICAL

### 2.1 Structure consideration of silicate melts

Three types of oxygen in silicate melts, bridge oxygen $O^0$, non-bridge oxygen $O^-$ and free oxygen $O^{-2}$ were first introduced by Fincham and Richardson /12/. The three types of oxygen are in a chemical equilibrium:

$$2O^- \Leftrightarrow O^0 + O^{2-}$$

The equilibrium constant $K_1$ is

$$K_1 = \frac{(O^0)(O^{2-})}{(O^-)} \qquad (1)$$

$(O^0)$, $(O^-)$ and $(O^{-2})$ are the equilibrium number of moles of bridge oxygen, non-bridge oxygen and free oxygen per mole of silicate melts.

Toop and Samis /11/ proposed that $K_1$ is a constant at a given temperature and characteristic of the cations present in any binary or ternary silicate melts. Thus, the number of moles of three types of oxygen can be calculated as follows.

$$(O^-)^2(4K_1 - 1) + (O^-)(2 + 2N_{SiO_2}) + \\ + 8N_{SiO_2}(N_{SiO_2} - 1) = 0 \qquad (2)$$

$$(O^0) = \frac{4N_{SiO_2} - (O^-)}{2} \qquad (3)$$

$$(O^{2-}) = (1 - N_{SiO_2}) - \frac{(O^-)}{2} \qquad (4)$$

where $N_{SiO_2}$ is the moles of silica.

The integral free energy of mixing is:

$$\Delta G_{mixing} = G_{mixing,anionic} = \frac{(O^-)}{2} RT \ln K_1 \qquad (5)$$

Ottonello *et al* /10/ correlated the equilibrium constant $K_1$ with optical basicity $\Lambda$ through the following equation.

$$K_1 = \exp[4.662 \times \left( \sum_i X_{M_i^{v+}} / \Lambda_{M_i^{v+}} - \\ - \sum_j X_{T_j^{\eta+}} / \Lambda_{T_j^{\eta+}} \right) - 1.1445] \qquad (6)$$

where $X_{M_i^{v+}}$ and $X_{T_j^{\eta+}}$ are the atom fractions of network modifiers and network formers in one mole of silicate melts. For binary silicate system, $X_{M_i^{v+}}$ and $X_{T_j^{\eta+}}$ are unity.

Thus, the content of three types of oxygen and integral Gibbs energy of mixing for binary silicate melts can be calculated by Eqs. (2)-(6).

It is noted that the optical basicity values show some discrepancies especially for FeO and MnO/14,15/. The theoretical optical basicity values calculated using Pauling electronegativities by Gaskell /13/ are adopted in the present work and shown in Table 1. The values were successfully applied to correlating phosphorous capacities with optical basicity. Ottonello *et al.* /10/ also used similar optical basicity values to obtain Eq.(6). Nakamura *et al.* /14/ proposed different theoretical optical basicity values based on average electron density. Their values are not used in the present work for consistency with Eq.(6).

**Table 1**

The optical basicity values for various oxides

| Oxide | CaO | FeO | MgO | MnO | $SiO_2$ |
|---|---|---|---|---|---|
| $\Lambda$ | 1 | 0.51 | 0.78 | 0.59 | 0.48 |

### 2.2 Estimating density from integral Gibbs free energy of mixing

The density of melts $\rho$ was calculated by the following equation:

$$\rho = \frac{\sum x_i M_i}{V_m} \tag{7}$$

where $V_m$, $x_i$ and $M_i$ are molar volume, mole fraction and mole mass of component i, Therefore, the main task that we faced is estimation of molar volume.

Analogous to the correlation between integral enthalpy of mixing and mixing molar volume by Ref. /4/, the molar volume can be calculated by the following equations for binary MO-$SiO_2$ system:

$$V_m = x_{MO}V_{MO} + x_{SiO2}V_{SiO2} + V_{mix} \tag{8}$$

while

$$V_{mix} = \lambda(x_{MO}V_{MO} + x_{SiO2}V_{SiO2})\Delta G_{mix}/RT \tag{9}$$

where $V_{MO}$ and $V_{SiO2}$ are molar volume of MO and $SiO_2$. $V_{mix}$ is the molar volume of mixing for MO-$SiO_2$. $\lambda$ is a constant for a binary system, but for different binary systems, $\lambda$ can be various.

$\Delta G_{mix}$ is calculated by Eq. (5), thus, $V_m$ can be acquired. Then, the density of binary systems can be calculated by Eq. (7).

## 2.3 Density estimation for ternary systems

Richardson /15/ proposed that ternary system AO+BO+$SiO_2$ can be treated as the ideal intermixing of AO $ySiO_2$ and BO $ySiO_2$. In this work, the molar volume of ternary or higher order system can be calculated with values of corresponding $M_iO \cdot ySiO_2$ system.

$$V_m = \sum_i (X_{M_iO} / (\sum_j X_{M_jO}) V_{M_iO \cdot ySiO2}) \tag{10}$$

where $V_{M_iO \cdot ySiO2}$ was calculated by setting $X_{M_iO}$=1-$X_{SiO2}$.

For example, for values for CaO-MgO-$SiO_2$, the system can be expressed as follows,

$$\begin{aligned} V = {} & X_{CaO}/(X_{CaO} + X_{MgO})V_{CaO \cdot ySiO_2} + \\ & X_{MgO}/(X_{CaO} + X_{MgO})V_{MgO \cdot ySiO_2} \end{aligned} \tag{11}$$

where $V_{CaO \cdot ySiO_2}$ and $V_{MgO\ ySiO_2}$ are calculated by setting that $X_{\text{"CaO"}}$ and $X_{\text{"MgO"}}$ equal to 1-$X_{SiO2}$.

## 3. RESULTS

### 3.1 Data of pure oxides

***(1). $SiO_2$***

The experimental density data of $SiO_2$ were given by Bacon /16/.

$$\rho(SiO_2) = (2.566-0.000213\ T) \times 10^3,\ (kg/m^3)$$

For molar volume, we have

$$V_m(SiO_2) = (22.5414+0.002757T) \times 10^{-6},\ (m^3/mol)$$

***(2). FeO and CaO***

The density data of FeO show a large diversity. The reason may be that the melt often contains more or less $Fe^{3+}$or iron. Also, due to the high melting point of lime（$T_m$=2885K）, the density of pure CaO has not been yet found. In Ref /17/, CaO-$Fe_2O_3$-FeO system has been considered to exhibit an ideal behavior. In such a system, the molar volume data were obtained using the linear summation of the partial molar volumes of the three pure components. The linear equations are shown below /17/:

$$V_{m,\ 1673K} = (15.59x_{FeO} + 18.50x_{FeO1.5} + 21.08x_{CaO}) \times 10^{-6}\ (m^3/mol) \tag{12-1}$$

$$V_{m,\ 1773K} = (15.83x_{FeO} + 18.65x_{FeO1.5} + 21.13x_{CaO}) \times 10^{-6}\ (m^3/mol) \tag{12-2}$$

$$V_{m,1873K} = (15.84x_{FeO} + 18.82x_{FeO1.5} + 21.62x_{CaO}) \times 10^{-6}\ (m^3/mol) \tag{12-3}$$

The above equations fit the experimental molar volume data of CaO-$Fe_2O_3$-FeO system well. In the present study, a concept of hypothesized molar volume for pure components had to be employed. The partial molar volume data of FeO and CaO in /17/ had to be used as the hypothesized molar volumes of the same pure components. From Eqs.(12-1)-(12-3), we obtained:

$$V_m(FeO) = (13.53708+0.00125\ T) \times 10^{-6},\ (m^3/mol)$$

$V_m(CaO) = (16.48957 + 0.0027\,T) \times 10^{-6}$, ($m^3$/mol)

***(3) MgO and MnO***

There is no experimental data for the molar volume of liquid MgO and MnO because of high melting temperature. The partial molar volume of MgO and MnO proposed by Mill *et al.* /3/ are accepted for the present work.

$V_m(MgO) = (16.1 + 0.00161\,(T-1773)) \times 10^{6}$, ($m^3$/mol)

$V_m(MnO) = (15.6 + 0.00156(T-1773)) \times 10^{-6}$, ($m^3$/mol)

## 3.2 Density estimation

The $\lambda$ values were optimized using experimental data for binary systems. The values are shown in Table 2. The comparison between estimated and experimental values /18,19/for $CaO-SiO_2$ system is shown in Fig. 1. It can be seen from the figure that the estimated values agrees well with the measured ones.

**Table 2**

$\lambda$ values optimized in this work

| System | $CaO-SiO_2$ | $FeO-SiO_2$ | $MgO-SiO_2$ | $MnO-SiO_2$ |
|---|---|---|---|---|
| $\lambda$ | 0.03 | 0.05 | 0.02 | 0.025 |

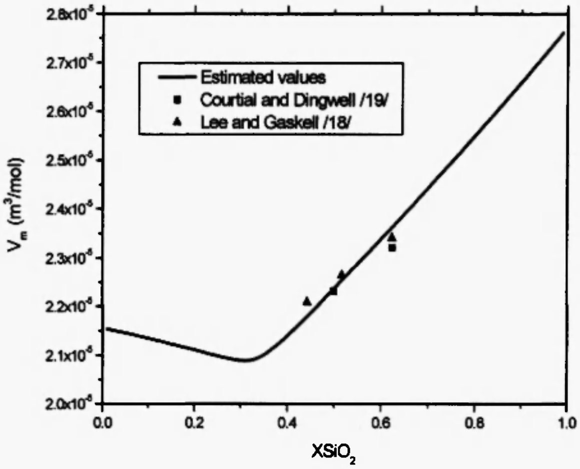

**Fig. 1:** A comparison between estimated and experimental values for $CaO-SiO_2$ system at 1873K

The comparisons between estimated and measured values for $FeO-SiO_2$, $MnO-SiO_2$, $MgO-SiO_2$ systems /20-23/are shown in Figs. 2-4. As seen from the figures, experimental values are fitted well by the present model. Furthermore, the estimation by present model reflects the deviation from ideality of the systems properly. For example, the departure from ideal mixing is most outstanding for $CaO-SiO_2$ system (see Fig. 1).

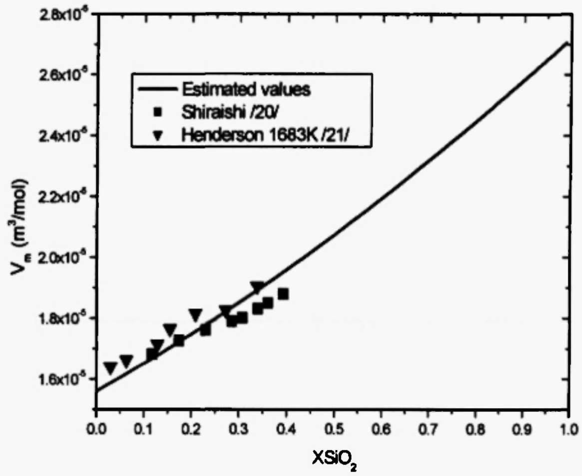

**Fig. 2:** A comparison between estimated and experimental values for $FeO-SiO_2$ system at 1673K

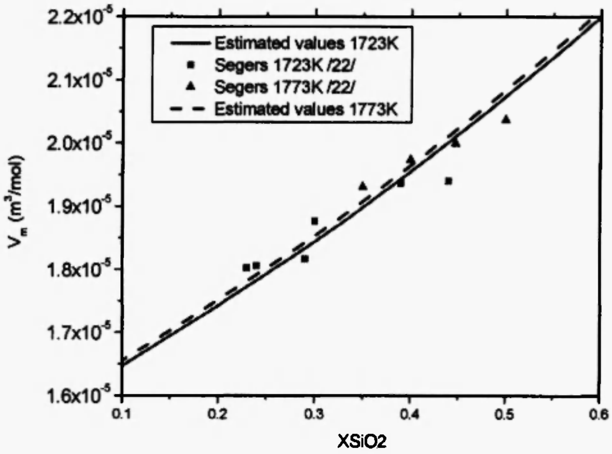

**Fig. 3:** A comparison between estimated and experimental values for MnO-$SiO_2$ system at 1723K-1773K

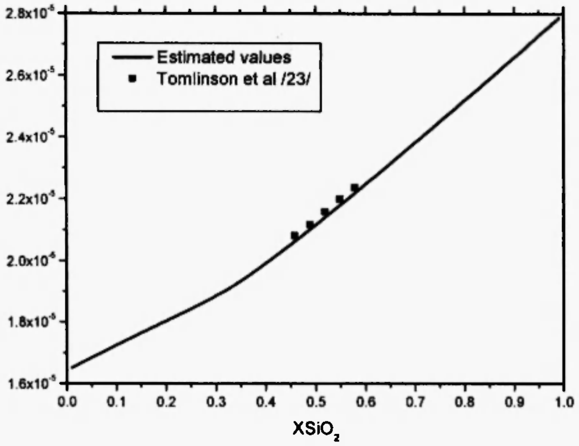

**Fig. 4:** A comparison between estimated and experimental values for MgO-$SiO_2$ system at 1973K

The molar volumes of ternary systems (CaO-FeO-$SiO_2$, CaO-MgO-$SiO_2$, CaO-MnO-$SiO_2$) were estimated using the present model. The comparisons between estimated values and experimental values /18,22, 24-26/ are shown in Figs. 5-9. It can be seen from the figures that estimated values agree with experimental values totally. Some deviations could be due to the scatter of experimental values. It can also be found that the present model provides more accurate values than idea mixing model.

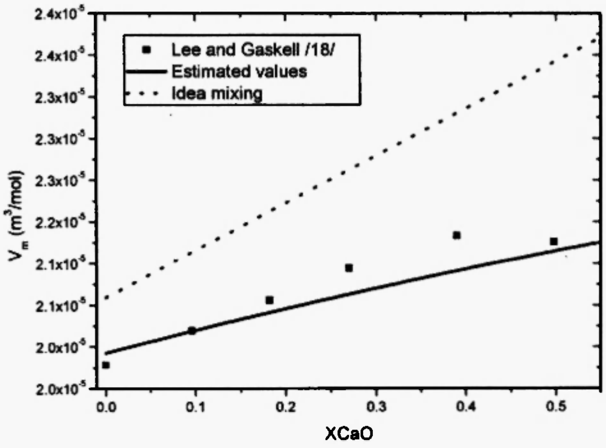

**Fig. 5:** A comparison between estimated and experimental molar volume values of CaO-FeO-$SiO_2$ system at 1873K with $x_{SiO2}$=0.44

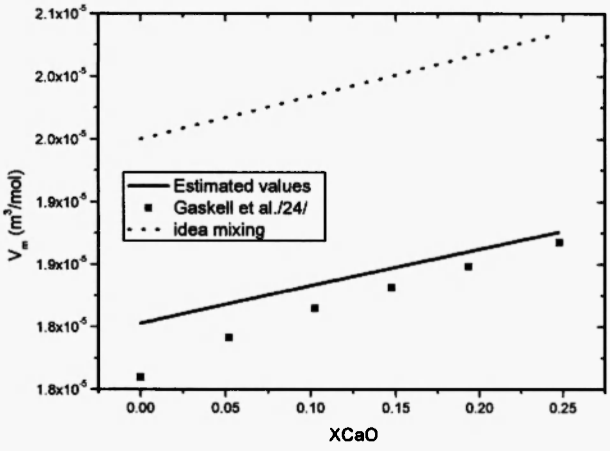

**Fig. 6:** A comparison between estimated and experimental molar volume values of CaO-FeO-$SiO_2$ system at 1683K with $x_{SiO2}$=0.3

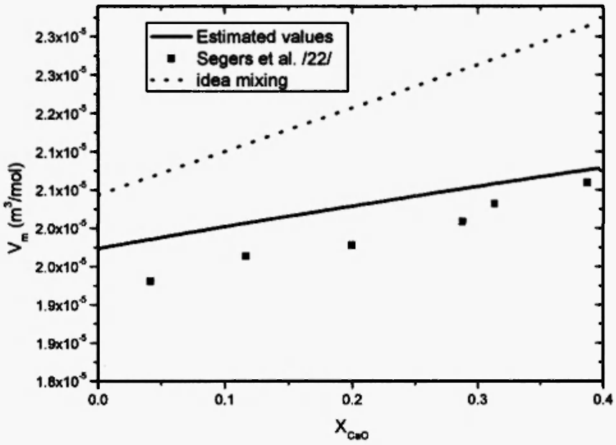

**Fig. 7:** A comparison between estimated and experimental molar volume values of CaO-MnO-$SiO_2$ system at 1773K with $x_{SiO2}$=0.45

The mean deviation $\Delta$ between estimated and experimental values is usually calculated as follows:

$$\Delta=\frac{1}{N}\sum_{n=1}^{N}\frac{|(V_n)_{\text{cal}}-(V_n)_{\text{mea}}|}{(V_n)_{\text{mea}}}\times100\% \qquad (12)$$

where $(V_n)_{\text{cal}}$ and $(V_n)_{\text{mea}}$ are the estimated and measured molar volume respectively. $N$ is the number of samples.

The mean deviation for the present estimation is within 3% totally, which is slightly higher than the experimental uncertainty (2%).

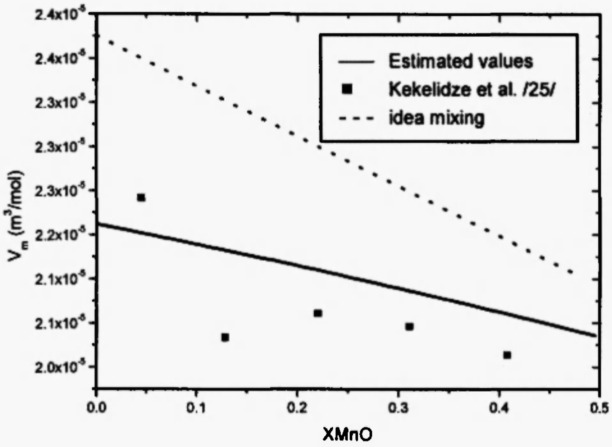

**Fig. 8:** A comparison between estimated and experimental molar volume values of CaO-MnO-$SiO_2$ system at 1773K with $SiO_2$ content of 40mass%

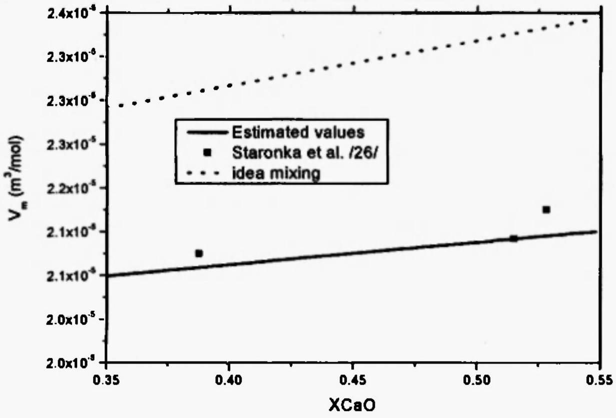

**Fig. 9:** A comparison between estimated and experimental molar volume values of CaO-MgO-$SiO_2$ system at 1773K with $x_{SiO2}$=0.44

## 4. DISCUSSION

Density of silicate melt is sensitive to change of melt structure. The deviation of molar volume from idea mixing behavior may be related to distribution of anions in silicate melts. In this work, this relationship was established through Gibbs free energy of mixing, which was calculated from the structural model by Toop and Samis. Optical basicity was adopted as the only parameter for calculation of Gibbs energy of mixing. The $\lambda$ values used in this work are close for different systems (except for FeO-$SiO_2$). Therefore, optical basicity is the predominant factor in the departure from idea mixing behavior of silicate melts. Actually, the results of Figs. 1-4 supported this viewpoint. It can be seen that the CaO-$SiO_2$ system has the most remarkable departure from idea mixing, while FeO-$SiO_2$ and MnO-$SiO_2$ system only have a slight departure. As can be seen in Table 1, the order of optical basicity of oxides is CaO>MgO>MnO>FeO. The extent of departure corresponds to the values of optical basicity. As pointed out by Mills /7/, the optical bascity of silicate melts could be a good structural parameter to measure the depolymerisation of melts. Therefore, the present model actually links density to structure of silicate melts by optical basicity. To some extent, the present model is an optical basicity model.

The present work assumes idea mixing of binary system to form ternary or higher order system. The present author has applied the method in viscosity estimation and has achieved a good performance /27/. For two binary systems AO-$SiO_2$ and BO-$SiO_2$, if the nature of $A^{2+}$ and $B^{2+}$ is close, e.g. $Ca^{2+}$ and $Mg^{2+}$, the method is proper to a large extent. When the nature of $A^{2+}$ and $B^{2+}$ is greatly different, e.g. $Ca^{2+}$ and $Fe^{2+}$, the present method will bring some errors in density estimation.

## 5. CONCLUSION

A model for density estimation of molten silicate slags was presented in this paper. Molar volumes of melts were estimated using integral Gibbs free energy of mixing, which can be calculated by the Toop-Samis model. Optical basicity was the only parameter in calculating integral Gibbs free energy of mixing. Comparisons between estimated values and experimental values have shown that the present model provides accurate values for silicate slags with a deviation within 3%. The present work established a relationship between density of molten silicate slags and structure of silicate described by optical basicity.

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